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NON METALLIC INCLUSIONS IN STEEL ORIGINS, TYPES AND DISTRIBUTION IN WROUGHT STEEL. PART 1.

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NON METALLIC INCLUSIONS IN STEEL

ORIGINS, TYPES AND DISTRIBUTION IN WROUGHT STEEL. PART 1

by

A.R. Palmer

ABSTRACT

The report provides a review of the types and origins of the non-metallic inclusions found in continuously-cast and ingot steel.

The steelmaking process and the composition of the steel are discussed as important influences upon the quantity and the type form and spatial distribution of the particles. The extent of deformation of the particles during hot-working processes is shown to depend upon their type and form and to govern the degree of anisotropy of the wrought steel in its ductility and toughness properties.

INCLUSIONS NON-MÉTALLIQUES DANS L'ACIER. 1ÈRE PARTIE: LEURS ORIGINES, TYPES ET RÉPARTITION DANS L'ACIER CORROYÉ

par

A.R. PALMER

RÉSUMÉ

L'auteur présente ici une revue des diverses sortes d'inclusions non-métalliques rencontrées dans l'acier produit en coulée continue ou en lingots, de même que des origines de ces inclusions.

On y présente le procédé de fabrication et la composition de l'acier comme des facteurs qui ont une grande influence sur la quantité, le type, la forme et la répartition des particules. On y démontre aussi que la déformation des particules pendant le façonnage à chaud dépend de leur type et de leur forme et détermine le degré d'anisotropie de l'acier corroyé en ce qui a trait à sa ductilité et à sa résilience.

INTRODUCTION

The Canadian Arctic and marine environments offer metallurgical challenges which are a special concern of CANMET, because of the severe conditions under which pipelines and automotive transportation must operate. Energy conservation through weight-reduction in automotive equipment and the special corrosion problems of the oilfields provide further incentives for improvements in steel properties.

In the Work Statement which has initiated the present review, J.D. Boyd wrote:-

> There are some problems with the toughness of concast slabs and plate which are related to the type and distribution of non-metallic inclusions. There is considerable work on the physical chemistry (of) steelmaking and casting ... and on the mechanical properties of plate products (but) little information on the effects of composition, steelmaking practice, casting variables and rolling conditions on the type and distribution of inclusions in the plate. This data is necessary to determine ... the relationship between inclusions and properties such as through-thickness ductility, resistance to sulphide stress-cracking and determination fracture"
>
> ("Non-Metallic Inclusions in Continuously-Cast Plate Steels", April 1983).

The present review describes the types of inclusions found in both continuously-cast and ingot steel: their origins, compositions, appearance and distribution. The literature on these topics is vast but the intention here is to provide a general perspective of inclusions and the influences of steelmaking, casting and hot-working upon them. A second part which is in preparation will review the role of inclusions in fracture processes and their effects upon the mechanical properties of steel.

A. Sources and Classification of Inclusions

1. General

Most of the particles described as non-metallic inclusions are formed when oxygen and sulphur react with other solute elements in liquid steel. Reactive solutes such as Mn and Cr are present as alloying elements. Al or Ca, on the other hand are added with the main purpose of complexing oxygen or sulphur. Silicon acts both as alloying element and as deoxidizer. A few oxide particles may be derived from extraneous matter such as fragments of refractory brick or hot-topping compound.

Nitrogen also forms insoluble compounds but these are seen only when Ti or Zr is present as an alloy addition or a residual element.

Carbide particles might be termed "non-metallic" but these are deliberately produced to enhance the mechanical properties of the steel product and are not thought of as non-metallic inclusions.

The metallic particles of lead or bismuth found in some free-machining steels resemble certain sulphide inclusions in shape if not in colour. These are simple dispersions of elements which are deliberately added and are not further considered in this review.

2. Reactions of Oxygen in Steel

Up to 0.23% of oxygen is soluble in liquid iron at 1600°C (1/III-12). Iron exposed to oxygen or the air will continue to react with that element, forming a liquid phase close to "FeO" in composition in the form of globules suspended in the liquid and as a surface slag (1/III-12; 8a). The dissolved oxygen is strongly held (in the atomic state) by the iron and the partial pressure of gaseous oxygen in equilibrium with the saturated solution is very small, at 10^{-8} atm. It is a fallacy to regard oxygen in iron or steel simply as a "dissolved gas" and to write it as "O_2".

Carbon added to the partly oxidized iron reacts to form CO gas and reduces the oxygen content to a much lower level. During ingot solidification, the segregation of carbon and oxygen in the residual liquid raises the local concentration and may initiate further reaction. The CO bubbles form blowholes which are seen in "wild" steel or the controlled "rimming" and semi-killed types.

Solutes such as Mn, Si and Al form condensed oxides and reduce the dissolved oxygen content to much lower levels. Blowhole formation is

suppressed but droplets or crystals of the oxides can remain in suspension in liquid steel and become entrapped in the ingot.

The distinction between dissolved oxygen and the oxygen present as suspended oxides is very important in the understanding of the origin of inclusions and of the three ways of expressing the oxygen content of steel:-

> Total oxygen content, as measured by chemical analysis or the neutron activation method, is the quantity of oxygen present both as dissolved oxygen and suspended or entrapped oxides.
> Soluble oxygen is that present in true solution. This quantity cannot be measured directly but for liquid steel a good estimate is obtained from activity measurements (see below) by allowing for the interaction effects of other solutes present.

The dissolved oxygen content of solid steel is extremely small because nearly all of it is precipitated by solutes such as Si and Al when the steel cools and solidifies. Even if we chemically extract and analyze the inclusions from solid steel and deduct the result from "total oxygen", the result will not represent the dissolved oxygen content of the liquid steel.

> Oxygen activity is the thermodynamic activity or chemical potential of the dissolved oxygen in liquid steel and can be measured by solid electrolyte cells ("direct oxygen probes"). It is usually written as "a_O" but the more correct symbol is "h_O" for Henrian activity. This takes no account of the quantity of suspended inclusions and bears no relation to the total oxygen content.

For carbon and low-alloy steels, there is no serious error in regarding the activity as numerically equal to the dissolved oxygen content. In principle, however, the quantities are not the same and in high-alloy steels, particularly when Cr is present, the activity is smaller than the dissolved oxygen content. (In stainless steel containing 18% Cr, the activity is as little as one-fifth of the dissolved oxygen content).

3. Reactions of Sulphur in Steel

Sulphur is freely soluble in liquid iron but forms FeS when the steel solidifies. The intergranular films have a strongly embrittling effect at hot-working temperatures, causing "hot-shortness". Manganese, which is present in almost all steels combines preferentially with the sulphur to form MnS. The resulting inclusions do not cause hot-shortness but can affect the ductility and toughness of the finished steel in certain patterns of stressing. The MnS particle-forms that can be tolerated will depend upon the applications of the steel.

The sulphur is derived initially from blast-furnace coke and until about 15 years ago, commercial steels typically contained up to 0.05% S and seldom less than 0.015%. (The AISE and SAE standards still permit 0.050% max in carbon steels and 0.040% in many alloy grades). The refining of blast-furnace hot metal and of liquid steel can now reduce the S content to levels below 0.005% and even below 0.002% for special requirements.

4. Classification of Inclusions by Composition and Appearance

The simplest categories are those of sulphides, nitrides and oxides. Inclusions of the first two types are normally easy to recognize. The "oxides" should, according to chemical principles, include such diverse forms as glassy silicates and clustered angular particles of alumina as well as the spinels and calcium aluminate compounds. For that reason the category is too broad to be useful although it appears in some industrial rating systems by which steel cleanness is routinely measured.

One system used in North American industry (ref. 5, Method C) makes a distinction between "oxides" and "silicates", to characterize angular undeformed particles and elongated glassy forms respectively. Another widely-used system (ref. 5, Method A) is more comprehensive, with four categories for inclusions in wrought steels:-

a) sulphide type;
b) alumina type;
c) silicate type;
d) globular-oxide type.

The terms describe particle shape rather than the supposed composition. Class B refers to angular inclusions in lines or "stringers", Class C to elongated glassy forms and Class D to dispersed undeformed particles. The German standard (6,7) has similar categories but subdivides them into single and grouped streaks, or according to particle size as distinct from the number of particles in a field.

Inclusion shape and colour are useful in routine quality assessments of commercial steel but in order to understand the origins and effects of the particles, the approach must be more analytical. "Globular oxides", for instance, might consist of dispersed alumina particles, calcium aluminates, small silicates or even small unidentified sulphides. The various compounds and their characteristics are considered in detail in Section B of this review.

5. Classification of Inclusions by Origin

The inclusions that are precipitated within the steel are described as "endogenous" (or sometimes as "indigenous") and can be divided into two categories:-

Primary: formed within the steel when absorbed oxygen reacts with certain solute elements or when deoxidizing elements are added;

Secondary: precipitated as the metal temperature falls within the ingot mould; the various types of manganese sulphide are also formed at this stage. (Refer also to Appendix A).

It was once common to refer to inclusions as "slag" or "dirt". There is no evidence that furnace slag is entrapped as inclusions: if this were so, the intense mixing in basic oxygen furnaces (BOF) and argon-oxygen decarburization vessels (AOD) vessels should result in very dirty steel. Sometimes, inadequate cleaning of an ingot mould introduces particles of sand; hot-topping compound or small pieces of ladle refractory may be washed into the teeming stream. These particles which are entrapped and not formed by reactions in the steel, are described as "exogenous" inclusions.

The distinctions cannot be rigidly observed however. Exogenous particles can become modified while suspended in the liquid steel or can act as nuclei for endogenous inclusions (I:III-1 and 2).

Whenever liquid steel is exposed to the air, oxygen is readily absorbed. In a ragged teeming stream, large particles of mixed oxides are formed as a result (52). According to the above classification these might be described as primary inclusions but it has become usual to put these into a separate class as "products of reoxidation". Some writers classify these products as "exogenous" but it is better to reserve that term for extraneous material which is simply entrapped.

B. The Common Inclusion Types

1. Sulphide Inclusions

Manganese sulphide, MnS, is found in almost every steel sample, unless the steel has been treated with rare-earth metals or calcium. The grey particles, which are familiar as longitudinal streaks in rolled sections, have a characteristic bluish tint and their colour is often described as "dove-grey". They are slightly translucent and sometimes show internal reflections from the interface with the metal (1/II-117).

Three distinct forms of MnS have been recognized and classified as Types I, II and III (2,12). the differences in morphology are caused by changes in the manner of separation from the liquid steel. All three types separate out from the interdendritic liquid at a late stage of the solidification process and may form by monotectic or eutectic processes (10,19; see also a review in ref. 1/IV-8). The oxygen content of the steel is the most important factor but other elements and the rate of cooling (14) also influence the sulphide type.

Type I MnS appears as scattered globular or ellipsoidal shapes which are not associated in chains or clusters. The particles often contain a second constituent which is not a single phase but a eutectic of MnS with MnO (11). In the as-cast structure, the particles may also show small cavities (11,12). This type of sulphide is seen only in steel which has a fairly high oxygen content, for example, in rimming and silicon-killed steels. At total oxygen contents above 200 ppm, Type I sulphide particles may be the only ones present but at lower contents (down to about 100 ppm) both Type I and Type II may be seen. At least 1% Mn is reported to be needed for Type I sulphide to be formed (12,16,20).

The hot plasticity of the particles is lower than that of the matrix. Single-phase particles can become somewhat elongated when the steel is hot-rolled, but much less so than the Type II particles. (This is discussed in more detail in Section D2, below). These sulphides sometimes form two-phase particles with glassy silicates (66) which became drawn-out as "tails" on the less-deformed sulphide particle as a result of hot-working. (1/II-Fig. 173; 3-Fig. 18-10).

Type II sulphide particles are those commonly found in commercial Al-killed steel and appear in the as-cast structure as intergranular chains of rounded or elongated particles. Deep-etching reveals fan-like arrays of rods or of branched shapes (12,13,17).

This type of MnS is plastic at hot-working temperatures and becomes drawn-out to long thin plates or threads, depending on the shape and size of the rolled steel section (11,13,20,56; see also Section D2, below). The elongated inclusions greatly reduce the ductility and toughness of steel when it is stressed in the transverse and through-thickness directions.

Type II sulphide particles are often found in close association with alumina particles and clusters. The sulphide may even enclose small alumina particles (1/II-Fig. 175). The association of sulphide particles with banded ferrite and pearlite is discussed in Section C5 of this review.

Type III particles exhibit the angular shape of octahedral sections and are present only in steel that has a very low content of dissolved oxygen (2,12). This type is formed when the residual content of soluble Al is high (probably at least 0.04%). A low oxygen content is not the sole condition. C and Si are reported to contribute (12) and the writer has observed these shapes in laboratory ingots of rail steel (0.7% C, 0.4% Si 0.9% Mn). This is believed to be an effect of the lowered freezing temperature (17) or of reduced solubility of S in the melt (19). Type III particles are therefore not found in unalloyed or low-alloy ingot steels in the lower-C range unless the Al additions are well above the normal levels for killing and grain-size control. Large Al additions are made to steel for castings so that the embrittling intergranular Type II particles are replaced by those of the dispersed Type III. The Type III sulphides are also found in high-Cr and high-Si steels and in cast-iron.

These particles, in spite of their crystalline appearance, are plastic at hot-working temperatures and have the highest deformability of the three sulphide types (11,13; see also Section D2 of this review).

Other types of sulphide particle have been described but the numbering does not appear to be universally accepted. Some writers have assigned "Type IV" to anchor-shaped and "Chinese script" forms found in cast irons (10) but another uses the same number for simpler shapes seen in a Ti-bearing steel (1/IV-12;18). Sub-categories such as IIR and IIF have been proposed for attenuated shapes seen in some alloys which have Mn and Cr contents above 2% (19).

When sulphide particles form in the solidifying ingot, they usually contain an appreciable amount of Fe substituted for the Mn. Just after solidification, the ratio Fe/Mn in the mixed sulphide (Fe,Mn)S is at least 1/4 and can exceed 1/1 (9,48,110,111). As the temperature falls, the equilibrium between the sulphide and the matrix changes in favour of more nearly pure MnS, so that Mn diffuses out of the adjacent matrix, causing some depletion of the Mn content in the vicinity of sulphide inclusions (110,111; see also Section C5 below).

Other elements which can be substituted for part of the Mn in alloy steels include Cr, Nb, Ti, V, Ni and Co (1/II-128; 9,48). The special case of calcium is discussed below.

Prolonged heating at temperatures above 1200°C causes elongated sulphide particles to become more spheroidal (13a), giving some improvement in transverse mechanical properties (115). Manganese sulphide has some solubility in austenite above 1150°C: at 1400°C as much as 0.005% S can be redissolved (13o). The latter temperature is higher than those normally reached in reheating for hot-working. When the steel cools after overheating, the dissolved MnS is reprecipitated as fine particles on the austenite grain boundaries. If the steel is fractured after hardening and tempering treatments, it exhibits large intergranular facets (13b). Severe overheating or "burning" may even fuse the MnS which is then able to penetrate the austenite grain boundaries and so cause tearing when the steel is hot-worked; the phenomenon can also occur in welds (1/III-101; 13b).

Zirconium in steel reduces the hot plasticity of sulphide particles either by modifying the MnS or by forming a separate compound. Several sulphides of Zr have been identified but in the usual case when only about 0.1% Zr is

present, the compound is likely to be ZrS which resembles MnS (1/II-139). It appears that there is an extensive series of single-phase sulphides with Zr substituted increasingly for Mn in MnS (21,54).

Zirconium was used in the development of HSLA steels to prevent hot deformation of sulphide particles and so reduce the anisotropy of mechanical properties (21-23). This eliminated cracking in severe cold-bending operations (21,23).

A carbo-sulphide $Zr_4C_2S_2$ has been identified in low alloy steels which contain 0.05 to 0.11% Zr (85-87). This was present either alone or in association with MnS as two-phase particles and is said to be plastic to some extent in hot-working (85,86).

Titanium sulphides are rarely seen in commercial steels. At low S levels (e.g., 0.01%) a Ti addition produces Type II sulphides which are less plastic than those of pure MnS (2,20). Several compounds have been described (1/III-137; 18) but the commonest form in steel is (Mn,Ti)S with only a small Ti content (9,20). Needles of TiS_2 have also been identified in steel (3) and other sulphides have been reported in Ni-based alloys (29).

Titanium has been used industrially as a sulphide modifier (23) but not on a large scale. Low-alloy boron steels may contain up to 0.06% Ti (to precipitate dissolved N) but there is no obvious effect on the form or deformability of the sulphide particles. At least 0.15% Ti is said to be needed for sulphide shape control (20).

Rare-earth metals form stable sulphides which are produced as primary inclusions when Mischmetall (about 50% Ce, 33% La etc.) or a similar mixture is added to liquid steel. Some of the particles are absorbed by the ladle slag, giving a desulphurizing effect but the amount of additive needed makes this procedure too expensive as a way of removing sulphur. The object instead is to precipitate the sulphur as non-plastic particles in place of MnS.

Cerium forms several sulphide compounds and an oxysulphide, Ce_2O_2S, which have the important property of not being deformable at hot-working temperatures (21,23-28,29). Other elements of the lanthanide series, which are also present in the commercial additives, form chemically-similar compounds (25,26) but their power to form useful compounds in steelmaking is not the same. Lanthanum is reported to be weaker than cerium in forming sulphide but stronger in forming the oxysulphide (25).

Rare-earth sulphides appear as rounded or partly-angular particles (23,24) which often consist of two or more phases and may include an aluminate (e.g., $CeAlO_3$). The colours are distinctive under the optical microscope (24a,29) but microprobe analysis is often needed for accurate identification.

The ratio of %Ce and %S in the steel for complete conversion of MnS to RE-sulphides should be at least 1.5/1 according to one writer (27) but others propose a ratio of nearly 3/1 (88). If the Ce content is too low, mixed sulphides of Mn and RE are formed which are plastic at high temperatures (24b). Inadequate deoxidation of the steel prior to the REM addition may yield complex oxides of RE with Al or Si, some of which can form clusters similar to those of alumina (I/II-30 to 36; 90).

Calcium forms the sulphide CaS which is much more stable than MnS. It is precipitated as dispersed particles and is not deformed when the steel is hot-worked. The particles often enclose smaller ones of calcium aluminate (see Section B4) or at low sulphur levels, each aluminate particle may have small areas of the sulphide attached to its rim (30-39).

By thermodynamic principles, a concentration of as little as 50 ppm Ca should form almost pure CaS in the presence of 0.3 to 1.0% Mn, the usual range for plate and structural steels. In practice, sufficient Ca must be present to form the compound at the given concentration of S: thus 0.008% S would require at least 0.010% Ca or 100 ppm.

The problem for the steelmaker is to introduce sufficient calcium into liquid steel. Simple additions of lump CaSi give very erratic results because of the low solubility of Ca in steel (0.03% max at 1600°C: Ref. 41) and the high vapour pressure of the element at those temperatures. Barium raises the solubility of calcium in steel (40) and the additives "Calsibar" and "Hypercal" were developed on that basis as deoxidizers and inclusion-modifiers (39). Republic Steel adds "Hypercal" to its "Cal-Deox" steel (42) for improved machinability, which is probably due more to the elimination of abrasive alumina than to any special properties of CaS. The two phase inclusions of CaS surrounding aluminate particles in these steels have been described as "bird's-eye sulphides".

The deep-injection processes (T-N, Scanlance) introduced in the mid-1970's, made it possible to introduce calcium into ladles of steel, in amounts which are adequate to remove much of the sulphur and to modify the sulphide (and alumina) inclusions (34,36,43,45,71). Large tonnages of strip

and plate could then be produced in which the mechanical properties - notably ductility and impact toughness - in the transverse and through-thickness directions were very nearly the same as those in the longitudinal direction.

Calcium can also be added in the form of wire in which the friable metal is sheathed with iron or aluminum and projected rapidly into the ladle. Sulphide-modification is achieved but the desulphurizing effect is small (35,49).

Very few writers have stated the calcium contents of treated steel. Laboratory heats have been made with over 100 ppm Ca (31) but industrial heats generally have levels in the range 30-70 ppm (35,36,49,50). It has been stated that the S content should be not greater than 0.010% if complete conversion of the sulphides is to be achieved (20,32,36). A simple calculation shows that 70 ppm Ca could not react with more than 56 ppm S (0.0056%) and this makes no allowance for the 20 ppm Ca or more needed to form calcium aluminates (e.g., with about 30 ppm of oxygen).

It is not surprising that the conversion of MnS to CaS is often incomplete and that Mn is often detected in the sulphide. The two sulphides are miscible and the hot plasticity of the mixed compound appears to change progressively with the ratio S/Ca in the steel (32).

There is no obvious difference in colour between MnS and CaS but the latter is reported to be darkened by contact with water (I/II-143).

Magnesium also forms a stable sulphide MgS. The metal is widely used for desulphurizing blast-furnace hot metal but its high vapour pressure at steelmaking temperatures introduces safety hazards. Mixtures of Mg granules with lime were successfully injected in the 1950's to desulphurize arc-furnace heats (46,47). Laboratory melts and a few industrial heats have been injected with a "slag-powder" which contained metallic Mg (44,45). The finished steel contained about 20 ppm Mg. Both MgS and MnS were present, giving particles of low hot-plasticity (44).

Chromium can replace part of the Mn in MnS (9,48). Its sulphide is reported to appear as a second phase under some conditions (I/II-140; 3) and to be plastically deformable. In stainless steels, which contain 10-22% Cr, there is no obvious change in the appearance of MnS which might be attributed to Cr.

2. Silicate Inclusions

The term "silicates" is usually understood to mean the globular particles (other than sulphides) seen in steels which have been deoxidized with silicon but have not had Al additions. These are more or less translucent and being amorphous, i.e., glassy, undergo progressive softening at high temperatures, so that most forms are quite plastic when the steel is hot-worked. Crystalline forms such as mullite ($3Al_2O_3.SiO_2$) are also "silicates" but are seldom seen in steel except as a second non-metallic phase within large glassy inclusions (see Section B7).

The primary inclusions found in suspension in Si-deoxidized liquid steel can be regarded as combinations of various metal oxides with silica. The silicates of Mn and Fe are the most common but several other elements may be present in the particles. Those of Al, Ca and Mg are often present, even when these elements have not been added to the steel, probably because of reactions with refractory materials. Oxides of Cr are detected in the silicates found in some alloy steels.

Under the microscope, the translucent particles show internal reflections which can be mistaken for a second non-metallic phase. These are due to the smooth, almost hemispherical interface with the matrix. The "Maltese Cross" pattern seen under polarized light has the same origin in the shape of the particles.

Pure silica does not appear as primary inclusions in commercial steels but its crystal form, cristobalite, is sometimes precipitated as dendrites within a large primary silicate particle (1/I-17 to 23). The presence of quartz is said to indicate an origin in refractory material i.e., an exogenous inclusion (ibid, p 25). Small clear globules which may be of almost pure silica are sometimes seen in hot-worked steel close to the scale layer and are due to solid-state diffusion of oxygen (51).

Crystalline silicate compounds can also form as secondary phases within primary glassy silicates, giving complex inclusions of two or more phases (1/I, passim).

Large silicate globules can be produced by reoxidation during ingoteeming (52). These are found even in Al-killed steel because exposure of metal droplets to the air oxidizes their entire Al content, after which part of the Si is also oxidized. When the droplets fall back into the pool, there may not be time before solidification to re-establish local equilibrium with dissolved Al there.

Most low-alloy steels contain about 0.20 to 0.35% Si but levels down to 0.10% are permitted for plain low-carbon grades. A heat of alloy steel made in the arc-furnace and argon-stirred in the ladle without Al-deoxidation might have a final oxygen content (total) of 80-150 ppm, corresponding to a silicate inclusion volume of about 0.05-0.08%.

The plasticity of most silicates during hot-working allows them to become highly elongated and their effect on transverse and through-thickness mechanical properties is much the same as that of sulphide streaks (see also Section D). Large silicate globules can produce visible lines on rolled strip. These are particularly detrimental in stainless steel intended for household appliances or architectural finishes.

Certain silicate glasses which contain lime and alumina and correspond to the anorthite composition (4:Fig. 80) have been found to reduce tool wear in high-speed machining. These soften sufficiently to flow and coat the tool tip at the high local temperatures of the cutting point (55-57).

Alumina

Aluminum is the most widely-used deoxidizer in the steel industry because of its cheapness and its properties of producing low oxygen levels in the steel and a fine ferritic grain structure in the heat-treated end product.

Alumina is a very stable oxide with an extremely low solubility in liquid steel. Thermodynamic data predict that 0.02% of soluble aluminum in the steel (i.e., not already in combination as the oxide) should limit the oxygen activity to about 1.5 ppm. In practice this theoretical level is not reached and activities of 3 to 6 ppm are measured with the direct oxygen probe. Suspended alumina particles will account for an additional 25 to 50 ppm of oxygen in a chemically-analyzed sample (see also Appendix D).

Alumina inclusions separate out of liquid steel quite rapidly through absorption into the slag layer and on glazed refractory surfaces, following chance contacts. The term "floating-out" which is often used is misleading because the small particles would rise very slowly by natural buoyancy and not at all in a liquid which is stirred by gas-bubbling or even by natural convection.

The steel does not usually become cleaner as a result of holding in the furnace or ladle because new particles are continually forming as oxygen from the atmospheric dissolves at exposed surfaces and reacts with the soluble aluminum. This process of "reoxidation" becomes severe during ladle-filling

and ingot-teeming, when the stream of liquid may be ragged and there is splashing in the pool (52).

Alumina in steel takes the form of hard crystalline corundum. It appears in polished sections as particles which are almost equiaxed and have a somewhat angular outlines often described as "sub-angular". The particles appear to be dark grey but may be translucent enough to show faint internal reflections. They commonly occur in loose clusters or "galaxies". The reason for this form of agglomeration has long been debated but scanning electron microscopy applied to deeply-etched sections has revealed that the particles are in fact cross-sections of loosely dendritic growths or coral-like masses which have grown from a common nucleus and constitute a single crystal even though it is not of a compact geometrical shape (58-60). Other crystal forms are possible and samples taken from steel within a minute or two of an Al addition may show tabular shapes which can appear lath-like in cross-sections.

An Al addition can decompose suspended liquid silicates in the steel. Under some experimental conditions when the Si content is high and the Al addition is small, the alumino-silicate mullite may appear (33) but in fully-killed steel the reaction goes to completion and only alumina is found.

Nucleation of alumina by Fe-Mn oxides in Si-free melts has been reported and gives intermediate products of Fe-Mn spinels (see Section B5). Under some conditions these can remain as traces within alumina particles (58,60) but if the ladle of steel is held for 10-20 min, the dissolved Al can decompose the spinels (61).

In rolled steel, the clusters become elongated and appear in longitudinal sections as "stringers" or narrow bands of alumina particles which have several detrimental effects upon the steel:-

a) excessive tool wear during machining, through abrasion by the hard particles;
b) poor machined finish because of tool wear and because of pitting and direct abrasion by dragged-out particles;
c) initiation of fatigue fractures, particularly in ball-bearing races and
d) anisotropy of mechanical properties, giving low ductility and impact toughness in the transverse and through-thickness directions.

It is important to distinguish between alumina and the aluminates, which are compounds of Ca (Section B4) or of Fe and Mn (Section B5).

4. Calcium Aluminates

When sufficient calcium is present in Al-deoxidized steel the clusters of alumina particles are replaced by dispersed particles of calcium aluminate. The calcium concentrations are similar to those needed to form calcium sulphide i.e., about 30-100 ppm and the two types of inclusion are often closely associated in the form of sulphide-coated aluminate particles. (The term "oxysulphide" has sometimes been used but these particles consist of distinct phases rather than a single compound which contains both S and O).

There are in fact five calcium aluminate compounds. If we write 'C' for CaO and 'A' for Al_2O_3, we can list these as follows:-

$$CA_6 \qquad CA_2 \qquad CA \qquad C_{12}A_7 \qquad C_3A$$

These are illustrated in references 31 and 48.

The phase diagram for the system lime-alumina (4,31,48) shows that adjacent compounds in this list form eutectics and that the combinations $CA + C_{12}A_7$ and $C_{12}A_7 + CA_6$ have the lowest melting temperatures*. The aluminates formed in liquid steel which contains 60-100 ppm Ca are usually those with the highest CaO content and the lowest melting point and are present as glassy globules. In steel with less than 50 ppm, aluminates of higher melting point are formed and have more angular, crystalline shapes (31). The two aluminate phases in a given eutectic are not easily distinguished but special etchants can show up the difference (1/III-114).

Calcium improves the machinability of steel primarily by eliminating the abrasive alumina clusters. All five aluminate compounds occur as small, dispersed particles which are not deformed by hot-rolling. There is then very

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* Various versions of the phase diagram disagree on which of these two eutectics has the lower melting point but the difference is small in either case.

little adverse effect upon the transverse and through-thickness properties of heavy plate or rolled strip. The total oxygen contents of Ca-treated steel, measured on ladle samples, are generally in the range of 15-35 ppm (34,45,50).

5. Spinels

The mineral "spinel" is magnesium aluminate $MgO.Al_2O_3$ but the term is more generally used to describe compounds of the type:-

$$R''O.R'''_2O_3$$

where R'' is a divalent element, e.g., Fe, Mn, Mg;
R''' is a trivalent element, e.g., Al, Cr.

The compounds form octahedral crystals and are isomorphous so that different elements in each valency group can be substituted for each other, either partly or completely (1/I-31; 62,63). For example, a continuous series of compounds is possible between hercynite, $FeO.Al_2O_3$ and galaxite, $MnO.Al_2O_3$. Compounds of this series may form when Al is added to steel which has a high oxygen content; if the steel has a high Mn content, the spinel will be richer in MnO (62). With larger Al additions, the spinels are decomposed and the residue is mainly alumina but some spinel may be present as a non-equilibrium phase (8a, 58,63).

Calcium aluminates belong to a different crystal system and are not included among the spinels.

Crystalline shapes, often described as "chromite" are seen in stainless steels which have been exposed to stream reoxidation. These may consist of chromium galaxite ($MnO.Cr_2O_3$) or of true chromite ($FeO.Cr_2O_3$) (1/I-86 to 88;63). The distinctive angular shapes are those of octahedral sections and their grey colour has a characteristic tinge of purple. The crystals are sometimes present as a second phase within glassy silicates. Being hard, they stand out in relief from the silicate and the matrix in a polished section.

6. Nitrides and Carbo-Nitrides

Nitrogen is present in low-alloy steels usually in amounts of 0.005 to 0.015%. The contents of electric-arc furnace steels are in the upper half of that range. High-Cr grades such as stainless steels may contain more than 0.030%. This constituent of steel should not be regarded simply as a "dis-

solved gas" (or written as "N_2") because very little can be extracted from liquid steel in a vacuum unless large volumes of CO are generated by oxygen-lancing to help purge out the nitrogen.

Titanium forms the well-known cubic shapes of brassy-yellow colour, written as Ti(C,N) and described as carbo-nitride or cyanonitride (3). The nitride and carbide are reported to form a continuous series of solid solutions (3). Simple thermodynamic calculations suggest that the compound will normally contain very little carbide, even where the C/N ratio of the steel is 50/1 or more.

The yellow crystals are seen in low-alloy boron steels which may contain 0.02-0.06% Ti and in Stainless 321 (e.g., 0.2-0.3% Ti). Scattered crystals also found in many steels which contain unintentional trace amounts of Ti and are often closely associated with the MnS inclusions indicating that they formed at a late stage of ingot-solidification. An agglomerated globular type of the carbo-nitride has been reported in strand-cast Stainless 321 (107).

Zirconium nitride also forms cubic crystals, which are stated to be paler in colour (3).

Aluminum nitride does not form in liquid steel but some may be precipitated as fine needles as the steel cools from about 1050° to 750°C. The crystals occur at primary austenite grain boundaries and are normally too fine to be seen under the optical microscope. They have a strong embrittling effect and if steel is reheated slowly through, or held in the range mentioned, there is further precipitation which leads to deep tearing during subsequent hot-working (64,65). These precipitates are also responsible for "rock-candy fractures" in steel castings (65), when large additions of Al have been made to produce the Type III sulphides.

Edge-cracking in rolled slabs of C-Mn-Al-Nb grades has been traced to grain-boundary precipitates of niobium carbo-nitride (104).

7. Multiphase Inclusions

Several examples of two-phase inclusions have already been mentioned:-

MnO and MnS in Type I sulphides;
Alumina particles within MnS;
Silicates attached to MnS;
Ca aluminates with CaS coating.

The glassy silicates, in particular, frequently enclose crystalline phases such as alumina laths, spinels and mullite (ref. 1; parts I & II, shows many examples with detailed identifications).

It is often suggested that the crystalline phase acts as a nucleant for subsequent formation of the phase that later surrounds it but one might expect that structural dissimilarity would make such a process difficult in many cases (although "heterogeneous nucleation" is a recognized phenomenon). Any phase diagram for mixed oxides shows that a single liquid phase can separate during cooling into several phases. The final structure then consists of distinct crystalline phases, sometimes in a glassy matrix (e.g., ref. 4). There is also evidence that CaS is soluble in a liquid $CaO-Al_2O_3$ phase and is precipitated as a separate phase when the aluminate solidifies (80).

Silicates which appear as a single glassy phase in ingots are often only metastable and the process of reheating for hot-working or heat-treatment may cause additional phases to be precipitated (1/I-58,59). Excess silica sometimes separates out, probably during ingot solidification, as cristobalite in dendritic shapes (1/I-19 and 24) or as compact crystalline forms (91). Identification of crystalline phases in polished sections is assisted when the harder particles stand out in relief (91).

The possibility of forming more than one sulphide phase when rare-earth metals are added to steel was mentioned in Section B1. Depending upon the degree of deoxidation of the liquid steel and the point of addition of the REM, complex compounds such as aluminates or oxysulphides which also contain Si or Al may also be present (90). Detailed examination with the electron microprobe is then necessary for complete identification.

C. Effects of Steel Composition and Manufacturing Processes

1. Steel Composition

The following paragraphs summarize the roles of added alloying elements and the common residual elements in forming inclusions and in influencing the internal quality of steel.

a) Direct contribution to oxide formation:-

Si, Mn, Fe: glassy silicates (which may also include smaller amounts of Al, Mg and Ca);

Cr, Mn, Al: spinels;

Al : alumina, calcium aluminates;

Ca : calcium aluminates.

b) Direct contribution to sulphide formation:-

Mn, Ca : well-known sulphide formers;

Cr : at high contents under certain conditions;

Ti, Zr : only if little or no free oxygen or nitrogen is present.

Rare-earth metals (the lanthanides): present only if specially added.

c) Direct contribution to nitride (or carbo-nitride) formation:-

Ti, Zr : added as alloying elements or as "getters" for nitrogen;

Al, Nb : submicroscopic nitride particles formed only in solid steel. (Nitrides of iron and chromium can be formed by special surface treatments or heat treatments of solid steel).

d) Elements forming metallic inclusions:-

Pb, Bi : added to enhance machinability - appear in the form of dispersed particles similar in shape and plasticity to Type II MnS particles, with which they are often closely associated.

(Note also that small concentrations of Pb, e.g., 0.003% or more, are detrimental to the hot-workability of some stainless steels although the particles are not visible under the optical microscope).

e) No contribution to non-metallic inclusions in steel:-

Alloys: Ni, Mo, W, V, Co (but all except Ni and Co can form carbide particles);

Nb: except as in item (c) above;

B : forms an iron borocarbide in solid state reactions. This inhibits the formation of pro-eutectoid ferrite at grain boundaries and so enhances the hardenability of the steel but is not seen under the optical microscope. B can also form oxides or a nitride but these are too small in amount or too strongly dispersed to be seen.

Residual elements:

P: may segregate at grain boundaries and contribute to temper-embrittlement and hydrogen embrittlement (81).

Cu, Sn: can contribute to poor hot-workability in carbon and alloy steels. An unusual tin-rich phase has been identified in a carbon steel ingot (67). Local concentrations of Cu and Sn can sometimes be detected by the electron microprobe in oxidized cracks or under scale layers on slabs but separate phases are rarely formed (124).

Zn: mostly lost as volatile oxide during steelmaking; not known to form inclusions.

As: soluble in solid steel; can cause temper-embrittlement but does not form inclusions.

2. Steelmaking in the Furnace

The types of inclusions found in finished steel are not directly affected by the choice of steelmaking process, whether in the open hearth, the basic oxygen or the electric arc furnace. Inclusion composition depends far more upon the composition of the steel, the choice of secondary refining process and of the final deoxider and other special additives.

The quantity of inclusions is governed by such factors as the following:-

Oxides - degree of oxidation prior to deoxidation (related to the "carbon drop" during decarburization and to the carbon content after that operation);

- concentration of FeO in the slag (although this is not an independent variable in a well-stirred system);

- extent of "blocking" by Mn and Si prior to final deoxidation, if any;
- opportunities for separation of suspended inclusions. (e.g., time and degree of stirring in the ladle);
- possibility of reaction with refractories, when an Al-killed heat is held in contact with siliceous material such as fireclay.

Sulphides - final S content of the steel. (The form depends upon the degree of deoxidation and the presence of additives such as Ca or rare-earth metals, as already described).

Rust and non-metallic debris in scrap charged to the melting furnace do not influence the quality of the final product. These are either reduced or absorbed into the slag well before the end of the steelmaking process. Some steelmakers believe that the large inclusions often found in ferro-alloys remain in the steel when the material is used as a late "alloy trim" addition but there is no clear evidence of this.

The highest qualities of steel for bearings and aircraft parts were formerly made in electric arc furnaces by a two-slag process. The widespread adoption of secondary refining processes, conducted outside the melting furnace or the BOF, has changed primary steelmaking and raised quality levels in the finished steel.

Carbon steels and low-alloy grades for large tonnage output are made in the BOF. The charge of blast-furnace hot metal can be pre-treated to remove sulphur, giving contents normally under 0.015% and frequently below 0.010%. Some Japanese operators are also dephosphorizing the hot metal to levels below 0.010%.

In spite of the vigorous oxidation in the BOF and the intimate mixing of metal and slag, the end product compares well in internal quality with steel made in other types of furnace. There is no entrapped furnace slag in the solid steel.

Basic oxygen furnace and electric arc furnace products differ in their ranges of nitrogen contents. The electric arc ionizes nitrogen from the atmosphere and facilitates its solution: a low-alloy grade usually contains 0.008-0.015% N. On the other hand, the purging action of the CO generated in the BOF tends to remove nitrogen so that steel from this furnace contains less than 0.010% N and possibly as little as 0.004%.

3. Secondary Steelmaking

In the last 15 years, industry has adopted a variety of processes for refining steel outside the melting or primary refining furnace. In simple vacuum-degassing, the steel is drawn up into a special vacuum vessel but in the other processes an adapted teeming ladle serves as the reaction vessel. There may be auxiliary equipment for stirring the liquid steel, injecting special reagents, supplying additional heat or applying a vacuum. The reactions of deoxidizing and desulphurizing are performed more efficiently than in the nearly-stagnant bath of an open-hearth or arc furnace. In addition the final adjustment of alloy composition can be made more accurately because of the more complete mixing.

Appendix B sets out the main processes and their key features. Their use is not confined to arc-furnace shops. Steel from open hearth and basic oxygen furnaces is degassed in Dortmund-Hoerder (D-H) and Ruhrstahl-Heraeus (R-H) vessels and desulphurized by powder-injection.

The changes in inclusion types caused by injecting calcium compounds have been discussed in Section B1 and B4 above. The processes that consist basically of vacuum treatment can reduce the number of oxide inclusions such as alumina but do not change the types of inclusions.

Argon-stirring in the open ladle causes the steel to circulate and brings the suspended inclusions into frequent contact with the slag, which absorbs them. Sulphur-removal is not possible, unless a very basic synthetic slag is added progressively during ladle-filling, because the exposed ladle-slag is semi-solid and is not intimately mixed with the steel once the ladle is full (76,77).

The ladle-furnace is a more recent development in which the argon-stirred ladle is covered and is provided with arc-reheating (70,78,79). The slag remains hot and fluid and the argon entrapped under the cover helps to reduce oxygen pick-up by the steel.

Vacuum-arc degassing (VAD) in the Finkl-Mohr or ASEA-SKF equipment produces the highest quality of steel that can be made without electrical re-melting of a cast or forged electrode. At very low pressures, the dissolved carbon decomposes suspended silicates and even alumina. The vigorous mixing of metal and slag by the expanding argon bubbles (supplied through a porous plug) facilitates the absorption of inclusions. With a lime-rich slag, sulphur levels below 0.005% can be reached.

These three processes usually have Al-deoxidation as a final step and the inclusions will consist predominantly of alumina and Type II MnS although the quantities are small. There is a risk that fresh alumina clusters will be formed by reoxidation of the teeming stream when the ingot-moulds are filled. This fact is becoming more widely recognized in North America and there is a movement toward more bottom-pouring, which offers better protection to the stream (see below).

Vacuum-degassing of liquid steel in D-H and R-H vessels is performed primarily for hydrogen-removal. Oxygen is also removed because the carbon-oxygen reaction is favoured by low pressures ("vacuum-carbon deoxidation") and many inclusions which are not decomposed become absorbed into the ladle slag because of the increased circulation of the steel. Only a small proportion of the nitrogen is removed, probably because the process of association and desorption of N_2 molecules at the metal/gas interface is slow (see also Section B6 above). Sulphur-removal is not possible because the slag does not enter the vacuum-vessel. The steel is sometimes only silicon-killed so that the residual inclusions are of glassy silicates and sulphides which are mainly of Type I. If a late addition of Al is made the inclusions are of alumina and Type II sulphide particles.

The vacuum-oxygen decarburization (VOD) process is used only for decarburizing stainless steel. Its effects in removing sulphur and oxygen (after the decarburization step) are similar to those of the VAD process. Stainless steels are not usually deoxidized with Al and the inclusions consist of silicates (sometimes associated with Cr-rich spinels - see Section B5) and Type I or Type II sulphide particles. Argon-oxygen decarburization (AOD) was developed to refine stainless steels at atmospheric pressure but has found widespread use for other grades, particularly in steel foundries. Vigorous mixing of a basic slag and the steel with argon gives good desulphurization and absorption of inclusions. The purging action of the generated CO in both the VOD and the AOD processes removes some of the nitrogen. The VOD vessel is used as a teeming ladle but steel refined in the AOD converter must be transferred to a separate ladle, with some risk of increasing the N and O contents by reaction with the air.

Powder-injection processes with Ca compounds have been referred to in connection with calcium sulphide and the aluminates (Sections B1 and B4). Their strong deoxidizing effect and the agitation at the ladle surface permits the absorption of hydrogen from atmospheric humidity. Increases ranging from

0.5 to nearly 2 ppm have been reported (36,82,83) and a subsequent vacuum degassing step is sometimes needed. Removal of S and O, which are both surface-active elements, reduces the barrier to the absorption of nitrogen from the atmosphere and increases in N content are in the range of 20 to 60 ppm (36,45,82,83). Even the injection of Ca wire gives a small rise in the H content of 0.3 ppm (49). A degassing step is sometimes added, particularly when the steel is to be strand-cast for the production of heavy plate.

4. Ingot Casting

The methods of casting and their effects on non-metallic inclusions are summarized in Appendix C.

Top-teeming is the method most widely practised in North America. The stream of steel and the splashes in the mould are exposed to reoxidation and it is difficult to devise equipment which will protect the steel under shop conditions.

Bottom-teeming of single or multiple moulds reduces the exposure of the stream to air. Air may be aspirated at the "trumpet" but shrouding devices with inert-gas purging can be attached to the ladle to minimize this. Because of the upward flow of metal into each mould, there is very little splashing and it is possible to add a fusible slag powder to give further protection and absorb oxide particles.

Many of the primary inclusions are eliminated if the ladle is held for 10 min or more between filling and ingot-teeming (127) and it is inferred that most of the oxides found in the ingot are products of reoxidation of the teeming stream and perhaps secondary inclusions, formed as the steel solidifies.

Segregation effects:

In the outer regions of an ingot, some inclusions are formed or entrapped between the arms of the columnar dendritic growths. The continuing rejection of oxygen, sulphur and other solutes into the residual liquid leads to the more concentrated precipitation of oxide and sulphide inclusions in the central region which constitutes "macro-segregation".

Oxide inclusions become attached to or entrapped in newly-formed crystallites in the liquid core and sink with them to form a "bottom cone of inclusions" in the lower central part (72,73). The particles may be either endogenous (126) or exogenous, the latter derived from material such as hot-

topping compound (73,74). When large ingots are to be forged into items such as turbine rotors, it may be necessary to reject as much as one-third of the ingot to eliminate this region of oxide concentration. One might also expect to find a denser distribution of particles toward one end of a heavy plate or strip made from an ingot (84).

In silicon-killed steel, a fairly wide distribution of particles smaller than 20 microns has been found but the larger particles were concentrated in the central zone (53). Silicate globules in the central zone may contain crystals of alumina or spinel compounds (66,68,126). Rare-earth oxides also tend to segregate into the "bottom cone" (28).

A sulphur-print of an axial section exhibits sloping lines where the MnS particles are concentrated. The "V-segregates" are close to the central axis and extend toward the bottom cone but are more strongly-marked in the upper part. The "A-segregates", which are longer and of opposite slope, lie outside these and are also more evident in the upper regions (28,72,89,130).

The steelmaker does not have much latitude for influencing the quantity and distribution of inclusions, once the steel has been refined, except through control of teeming temperature and (to a smaller degree) of mould temperature. A steep thermal gradient in the mould, due to a high teeming temperature and a cold mould, favours the columnar mode of crystal-growth and gives a greater degree of centre-segregation. A lower metal temperature and a warm mould results in an earlier transition from columnar to equiaxed crystallization and gives a wider dispersion of secondary inclusions but allows less time for primary inclusions and the products of reoxidation to separate out before they become entrapped.

Inclusions and "Banded Structures"

The banding of ferrite and pearlite in rolled steel is common and may be sufficiently strong to reduce the transverse and through-thickness strength of plate below the normal value or to affect the integrity of welded joints. Two types of banding must be distinguished: intermittent and periodic.

Intermittent banding consists of well-marked but irregularly-spaced streaks of ferrite. Elongated sulphide inclusions lie along the middle of each streak.

As the ingot cools, Mn diffuses from the matrix into the sulphide particles because the falling temperature favours the replacement of their FeS content by MnS (see Section B1). The local depletion of Mn in the matrix

causes carbon to diffuse away into regions of higher Mn content and away from the vicinity of the particles. When the steel temperature reaches the Ar_3 level, ferrite forms in the zone that is depleted of carbon (110,111). The sulphide particles themselves may act as nucleants for the ferrite (112). Mn atoms diffuse slowly and in heavy ingots where the cooling rate is lower, there is more time for diffusion and the banding effect is stronger.

The lines of sulphide particles that give rise to this banding have been traced to V-segregates (113) and it is likely that A-segregates would have the same effect.

Periodic banding is an effect of micro-segregation. When primary dendrites from iron of low solute content solidifies first and the solutes (both alloying elements and residuals such as sulphur) become concentrated in the interdendritic spaces (113,114). At the Ar_3 temperature, ferrite forms first in the cores of the dendrites and is responsible for the regular light-etching bands seen under the microscope in a rolled section. Oxide and sulphide inclusions formed in the interdendritic spaces are small and are usually enclosed by pearlite. The reaction of sulphides with Mn from the matrix is again possible but the resulting ferrite bands are narrower than those of the dendrite cores (114). It is reported that microsegregation is strongest in the equiaxed crystal zone, i.e., the central part of the ingot (113). Periodic banding would then be loosely associated with oxide inclusions present in the same region although not caused by them.

5. Strand Casting

The composition of the oxide inclusions is controlled basically by the final deoxidation of the steel and by any injection of reagents such as CaSi, as already described. The sulphides will correspondingly consist of MnS or CaS.

If there is secondary refining of the steel or even simple argon-stirring in the teeming ladle, most of the primary inclusions are eliminated and very few find their way into the mould (76). Any large inclusions found there are likely to be products of reoxidation because of the exposure of the turbulent liquid to the air, in the streams entering and leaving the tundish and in the tundish itself. Large silicates or spinels accumulate at the meniscus and become trapped in the cast surface but are not usually seen in commercial plate since they are either scaled off during reheating or cause rejection of the product prior to shipping. Some large entrapped inclusions

have been traced to ladle slag but these can enter only when the liquid level in the tundish is low during ladle-changes in sequence casting and are avoided by good tundish design and operating practices (102). Exogenous inclusions have in the past been traced to the tundish lining or other refractories but improved linings and design have eliminated most of these (99-101).

Steelmakers formerly experienced difficulties in casting Al-killed steel because alumina, formed by reoxidation, accumulated in the tundish nozzles and blocked them (97). Reoxidation problems have been overcome by enclosing the streams in refractory tubes, covering the tundish and excluding air by inert-gas purging (99,102,103). The injection of CaSi or similar reagents for desulphurization has the added benefit of replacing alumina inclusions with aluminates, which do not form accretions to cause nozzle-blockage (98). The oxides of rare-earth metals can also block the tundish nozzle (97).

If the nozzle-blockage and stream reoxidation can be eliminated by the measures mentioned, Al-deoxidation will reduce the quantity of secondary inclusions in the steel by reducing the dissolved oxygen content of the liquid to low levels (99) and the solid steel will be cleaner than ingot products (94).

The secondary oxide inclusions form throughout the cooling of the strand and are fairly well dispersed by entrapment among the growing crystals. In curved-mould machines, a band of inclusions accumulates on the "upper" side of the curve and is seen in the solid section at about one-sixth of the thickness from the surface which had the smaller radius (101,102,104).

The forced cooling of the strand produces a steep thermal gradient from surface to centre and favours columnar crystal growth. This accentuates the segregation of solute elements such as C, Mn, P, S and O into the residual liquid. Sulphide inclusions, which form at a late stage of solidification of the steel are then concentrated in the central region (94,109).

Columnar crystals do not advance with a uniform front and leading growths can bridge the centre, trapping a pocket of residual liquid. The intervals between bridges may be only 5 to 10 cm but each pocket of entrapped liquid solidifies as in a normal ingot and forms V-segregates, a small oxide-rich zone and often some shrinkage porosity. The recurring pattern has been termed "mini-ingots" (92,93,94,105). Phosphorus does not form non-metallic inclusions but local concentrations as high as 0.7% have been found (104).

The high ferrostatic pressure in the liquid core tends to expand the hot shell. The flexing, as the strand passes between support rolls, is sometimes sufficient to cause internal cracking between columnar crystals. The crack is refilled with solute-rich liquid and is marked in the solid strand by lines of sulphide inclusions, often enclosed in ferrite (96,106). This defect is difficult to eliminate and has been cited as a strong reason for pretreatment of the liquid steel to obtain S contents well below 0.005% (106,108).

In recent years, electromagnetic stirring has been adopted for improving strand quality. Rotary stirring in the mould is claimed to draw inclusions toward the centre, where they rise and can be absorbed by the mould slag (93) but there is a risk that some which rise too slowly will form a central band of oxide in the strand. Stirring farther down the strand mixes the liquid, reducing its thermal gradient and arresting the columnar growth (93,95). The resulting equiaxed crystallization eliminates the "mini-ingots" and distributes the inclusions more uniformly (93,95,105). Etched sections from the slabs frequently exhibit "white bands" or lightly-etched zones at the junction between columnar and equiaxed crystal regions. These are depleted in C, Mn, Si and other solutes (103,107) but have no adverse effect on mechanical properties of rolled products (93,107).

To make a given thickness of rolled plate, the strand-cast slabs applied would be thinner than ingots cast for the same purpose. In addition the section is rapidly-cooled on the casting machine to a temperature well below the Ar_3 level. The time available for the diffusion of Mn is greatly reduced and banding (Section C4 above) is minimized. Electromagnetic stirring, by dispersing sulphide particles, should further reduce the banding effect.

D. Deformation of Inclusions During Hot-Working

1. Relative Plasticity

The capacity of a given type of inclusion to deform plastically is expressed in relation to the deformability of the matrix.

If a round ingot is rolled to a round bar, inclusions which are initially spherical deform to ellipsoids. In these shapes, all plane sections parallel to the major axis have the same ratio of length to width:-

$$L/W = \lambda$$

If the length-to-width ratio of a deformed cubic element of the matrix is h, the relative plasticity for index of deformability is defined as:-

$$\nu = 2 \log \lambda / 3 \log h \qquad (11,20,116,117)$$

The highest value is 2.0, for a liquid inclusion. A value of 1.0 signifies deformation equal to that of the matrix.

For flat sections, the steel is deformed to different degrees in its width and thickness and the above expression must be modified (118,119).

The value of the relative plasticity is affected by the following factors:

- the composition of an inclusion;
- the presence of a second phase within it;
- the deformation temperature;
- the particles size;
- the degree of reduction of the steel.

2. Deformability of Manganese Sulphide Inclusions

MnS has a cubic structure of the NaCl type and pure crystals not enclosed in steel deform by slippage on certain preferred crystal planes (120). Inclusions which are exposed in a polished face of a steel specimen while it is deformed appear to behave as hard particles, pulling away from the matrix and fracturing. Those that are within the steel deform plastically at all temperatures down to sub-zero levels (125). The relative plasticity is different for the three sulphide types.

The simple angular shapes of the Type III sulphide particles give the impression that these are rigid crystals but in fact their plasticity is the highest among the three types. The relative plasticity increases as the temperature of hot-working falls and the numerical value approaches unity at the end of a hot-rolling operation (11).

Type I particles are much less plastic and the highest value for their relative plasticity has been reported as 0.64. It is thought that small amounts of oxygen dissolved in the MnS are responsible. On the other hand, the MnO-MnS eutectic which is often associated with Type I sulphides melts at 1232°C when pure and probably at lower temperatures in commercial steel: the liquid becomes drawn out during hot-rolling and forms "tails" to the associated MnS particles. At lower temperatures, the eutectic is more brittle than

the MnS particles and a Type I particle is then found to be surrounded with fragments of the darker eutectic (11).

Type I sulphide particles have higher plasticity at lower temperatures but some workers believe that there is a peak value after which plasticity falls with temperature and various critical temperatures between 800 and 1150°C have been proposed (Fig. 11 of Ref. 11 compares various sets of data; see also 111 and 119). All writers quote relative plasticity values of 0.60 or less at 1200°C, signifying that the inclusions are much less plastic than the matrix at high temperatures. One result is that conical voids may form at either end (in the rolling direction) of each Type I particle (11).

The relative plasticity of Type II sulphide cannot be reliably measured because the particles are not equiaxed in the cast steel. It is generally agreed that the value lies between those for Type I and Type III particles (1/III-71; 13). Hot deformation reorients the colonies of particles parallel to the rolling direction and they become greatly elongated and, in strip or plate, also flattened. Their plasticity decreases as the rolling reduction progresses and it is thought that the applied energy is absorbed by the increasing interfacial area so that less energy remains available to change the particle shape (11).

The effect of interfacial area has also been reported for Type III particles, where smaller particles in ingots were observed to have lower relative plasticity values (129).

It is possible to reduce the degree of elongation of MnS particles by rolling at as high a temperature as the steel allows. The low finishing temperatures of controlled rolling schedules may have the adverse effect of producing greater elongation of the particles. Deliberately raising the oxygen content of the steel to produce the less plastic Type I inclusions is not a good solution since this leads to a greater volume of silicate inclusions which are also plastic (11).

If a larger ingot is applied in making a given section of product, the following effects can be predicted:-

- the slower cooling will produce larger MnS particles;
- the heavier reduction to final size will elongate the particle more;
- finishing temperatures may be lower (in the longer reduction sequence) and cause greater elongation of the sulphide particles (11).

A continuously-cast bloom or slab for the same rolled product would probably be of smaller section than the ingot and would minimize those effects, in addition to having a finer dispersion of inclusions because of the more rapid solidification.

3. Deformability of Silicate Inclusions

Single-phase silicates, which are amorphous, soften from a hard brittle state to a plastic condition. This change has been reported to extend over a range of about 100°C (118) but another writer suggests a range of only 50°C (121). At higher temperatures, the silicates are at least as deformable as the matrix, with index values over 1.0 and reaching nearly 2.0 (116,118,121). Silicates in this condition become elongated during hot-rolling and form long thin streaks which are detrimental to transverse ductility and toughness. During heavy reductions, the streaks sometimes develop "necks" and break up into shorter lengths. Streaks lying side-by-side can fuse together (118).

The softening temperature depends upon silicate composition:-

$FeO-MnO-SiO_2$ inclusions (35-50% SiO_2) soften at 1000 to 1150°C;
$MnO-SiO_2-Al_2O_3$ inclusions (30-50% SiO_2) soften at 700 to 900°C.

but most of those containing more than 50% silica and little alumina (e.g., cristobalite, tridymite) soften at levels above 900° and may reach only moderate plasticity (ν = 0.4 to 0.9) (121).

Most determinations have given zero deformability at temperatures below the softening point (116,121) but one worker suggests that the brittleness is at a maximum just below that point and that a degree of toughness develops in the silicates at lower temperatures, with index values up to 0.45 (118). If steel is rolled at temperatures below the softening point of the silicate particles present; the particles may break up and form "stringers" of angular particles (116,118,122).

If a large hard particle remains intact during hot rolling, the forces acting at the interface with the matrix may initiate cracking in the matrix at the two extremities of the particle in the rolling direction. The pattern of metal flow opens these cracks to create conical voids (11,116,122). There are no reports that the cracking continues beyond this stage or that the voids serve to initiate failure during service stressing.

4. Behaviour of Other Common Inclusion Types

The following inclusions are not plastic and do not normally fracture during hot-deformation of the steel:-

Alumina;
Calcium aluminates (may be crushed: 1/II - 13);
Spinels (reported to deform slightly at above-normal temperatures: 1/III - 65);
Titanium carbonitride;
Titanium and zirconium sulphides;
Rare-earth sulphides, oxysulphides and oxides.

Pure silica is probably brittle enough to be fractured but its behaviour depends upon the crystal form (1/III - 66). Some calcium aluminates appear to be glassy particles but are not plastic at hot-working temperatures (33,123). Small particles are more resistant to deformation than large ones and this might be a factor in the case of aluminate particles, which are normally small.

Calcium sulphide is not plastic but if the Ca content of the steel is insufficient, the particles become elongated to some degree during rolling (33), because a mixed sulphide (Ca,Mn)S is formed (see paragraphs on calcium sulphide in Section B1, above).

5. Behaviour of Multi-Phase Particles

A plastic phase which surrounds a hard particle becomes elongated to form "tails" on either side of the core particle and an angular hard particle rotates to become better aligned with the rolling direction (118,123). The softer phase may even be stripped from the harder one (118) or, at lower rolling temperatures, the particle may fracture beginning at the interface between phases. When the softer material constitutes only a small part of the complex particle, the harder core has a stiffening effect and reduces its deformation (116).

E. Closing Comments: Limitations to the Cleanness of Steel

Liquid steel is never in equilibrium with its surroundings. True equilibrium would only exist if both steel and its container were converted to a mass of metal oxides with refractories fluxed into it. Fortunately for steelmakers, the reaction rates are low. Oxide particles must however be regarded as natural constituents of the multiphase material called "steel" and not as accidental contamination.

Steel is inevitably exposed to the atmosphere at many stages of the refining process and this imposes practical limits on the elimination of oxygen. There is probably no commercial refining process that consistently attains total oxygen contents below 15 ppm in low-alloy steels. Lower levels are reached only in VAD treatment of high-carbon bearing grades or by vacuum-arc remelting of alloy grades for critical applications.

Sulphur is derived from blast-furnace iron and from recirculating scrap steel. With deep-injection of powders into hot metal or finished steel, the steelmaker can now reach 0.002-0.003% S with confidence. Given sufficient process time, there is probably no lower limit (on a logarithmic scale) to the final sulphur content. Already Japanese producers are reporting levels of 5 to 10 ppm S in steel for sour-gas applications (128).

The impurities that cannot economically be removed from the steel must be converted to the forms that will be least harmful under the specific service conditions for the steel. The calcium treatments introduced during the last decade have been strikingly successful both in removing sulphur and in modifying sulphide and oxide inclusions to small dispersed, non-deformable particles. These processes have set new standards for steel refining and for the internal quality of tonnage steel.

There is still much to be learned on the practical control of inclusion composition and morphology. In any given grade of steel, the inclusions will always be too diverse in composition, shape and size distribution for a simple correlation of quantity with mechanical properties. Even for a well-defined type of inclusion there can be no fixed limits of size since its effect varies with its location in the pattern of service stresses.

As the dependence of failure mechanism on inclusion characteristics becomes better understood, it should nevertheless be possible to state the permissible types and quantities of inclusions more precisely in relation to the known service conditions of environment and stress and to set reasonable limits on the particles sizes.

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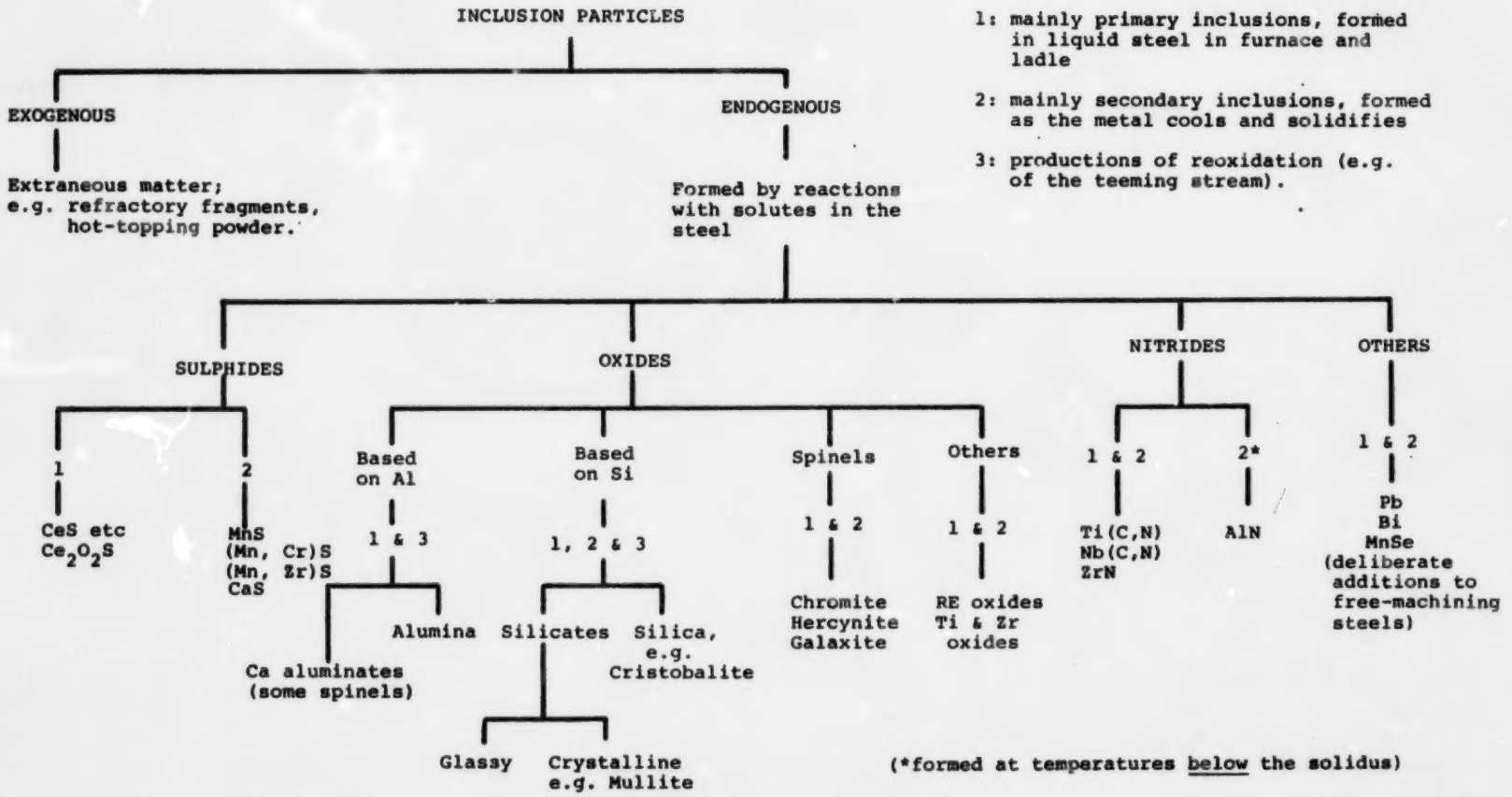
APPENDIX A A CLASSIFICATION SCHEME FOR INCLUSIONS IN STEEL



APPENDIX B - SECONDARY REFINING PROCESSES ("Ladle Metallurgy")

Process	Main features						Purposes			
	Argon stirring	Induction stirring	Arc reheating	Vacuum	Injection of solids	Degas (H)	Removal S	Deoxidize	Remove inclusions	Modify inclusions
"Argon-bubbling"	x						(e)	x	x	
Ladle-furnace	x		x				(e)	x	x	
Powder-injection $CaSi$, CaC_2 (a)	x				x		x			x
CaO etc. (b)	x				x		x			(f)
Wire-injection Ca (c)	x				x		8a			x
D-H & R-H (d)				x		x		8a	8a	
Ladle-to-ladle degasser				x		x		8a	8a	
Stokes degasser		x		x		x		x	x	
ASEA-SKF	sometimes	x	x	x		x	x	x	x	
Vacuum-arc degasser (Finkl)	x		x	x		x	x	x	x	

NOTES: 8a- Additional benefit in many cases but not the main purpose.

(a) - e.g., Thyssen-Niederrhein (also known as Calcium-Argon Blowing) and Scanlance.

(b) - e.g., Mannesmann, Kloeckner and others; includes spar and sometimes Al or other materials.

(c) - Calcium-cored wire with shell of steel or aluminum.

(d) - Dortmund - Hoerder and Ruhrstahl-Heraeus degassers.

(e) - some S-removal may be possible with synthetic basic slag if added to furnace tap.

(f) - conflicting claims (see Section C4).

APPENDIX C - CASTING METHODS: FACTORS INFLUENCING NON-METALLIC INCLUSIONS

Method / Factor	Ingots: Bottom pour	Ingots: Top pour	Strand-casting	Effect of factor on NMI: Type	Quantity	Location
Reoxidation	less	more	streams and tundish more easily protected	x	x	
Synthetic slag in mould	yes	no	yes (protects meniscus, absorbs inclusions)		x	
Deoxidizer to mould	e.g., CaSi to "trumpet"	rarely	Al wire injected into mould	x	?	
Segregation: MnS	V&A segregates		"Mini-ingots" with V segregates; filled cracks in columnar zone			x
oxides	Bottom-cone effect		Centre segregation; pockets in "mini-ingots"			x
Tundish design	-	-	Promote separation of inclusions, avoid air entrainment		x	
Angle of ports in mould-tube	-	-	Upward-angled jets assist contact of inclusions with mould slag		x	
Electromagnetic stirring	-	-	In mould-		x	
			Below mould-			x

APPENDIX D - TOTAL OXYGEN CONTENTS OF STEEL

The following data summarize results from a variety of sources (see special references which follow). In many instances the grades of steel were not stated but among the vacuum processes we can probably assume that the lowest oxygen contents refer to the grades of highest carbon content (e.g., SAE 52100 bearing steel). It is thought that the steel was deoxidized with aluminum.

Process (see also Appendix B)	Total oxygen, ppm		References (p. 47)
	Liquid steel	Solid steel	
Argon-stirred (open ladle)	25-80	20-50	A1 & 6, B1 & 2
Ladle furnace		10-35	A7, C2, D3
Ladle-to-ladle degassing		10-25	A2
D-H & R-H degassing	40-50	10-45	A1, 2, 3 & 6
Ladle/arc degassers*		8-40	A2 & 4, C1 & 2
Powder-injection	15-45	10-40	A5, B1, 2 & 3, D1 & 2

(* VAD, ASEA-SKF)

The data do not refer to the same grades of steel and we cannot compare the efficiency of the processes on this evidence. The results show only that the stated levels can be reached under certain conditions. In general it appears that levels below 40 ppm are frequently reached with suitable equipment but that it is very difficult to reduce the contents below 10 ppm. This might be due to reactions with ladle refractories or to reoxidation of the teeming stream.

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